Method of continuously measuring work function changes

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A method has been developed for measuring work function changes continuously. It is an ac variation of the diode technique and can be implemented easily in a standard retarding potential LEED/Auger system with derivative detection. Measurements for oxygen adsorption on an Ir single crystal illustrate that this method resolves work function changes within 5 meV.

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INTRODUCTION

Various surface phenomena, especially transient ones, may be studied both qualitatively and quantitatively through work function changes, or contact potential difference (CPD) measurements.[1] In implementing the CPD measurement, the diode[2,3] technique is used frequently. The theory of the diode method has been treated thoroughly[1-3] but will be reviewed here to reiterate its limitations. The system consisting of an emitter, an electron gun, and a collector, the solid surface on which the measurements are made, constitute an energy analyzer. When a fixed current (I_0) impinges on the surface that is biased negatively, the current collected at the solid (I) varies with the retarding potential (E_r) as shown in the diode curve of Fig. 1(a). Modifications of the surface potential shift the abscissa by an amount equal to the work function change. The first derivative of the diode curve, shown in Fig. 1(b), approximates the energy distribution of the impinging electrons. Since electrons scatter from the band gaps of the solid, additional structure may appear.[4] This structure does not influence the CPD measurement if it is a few volts distant from the crossover point (E_c shown in Fig. 1). The shape of the diode curve also varies with the angle of incidence of the incident electron beam onto the surface since the reflectivity of the sample varies with this angle.[3] These artifacts that distort the diode curve must be circumvented in implementing a diode method.

Techniques which monitor the CPD continuously are useful for examining nonequilibrium surface phenomena.[3] In continuous diode measurements, the collected current or a derivative of it is sampled to provide an error signal, which is used for modifying the gun potential or the retarding potential. The change in either potential reflects the CPD. Since dc techniques are plagued with noise and drift problems,[5] ac methods with derivative detection are preferred in continuous measurements. A sinusoidal voltage ($V_m \sin\omega t$) is superimposed on the gun potential, and, typically, the second harmonic of the gun current (i_2) is collected. If the width of the electron energy distribution (E_w) exceeds the sinusoidal modulation, the second harmonic is approximated closely by[6]

$$i_2(E_r) = (V_m^2/2)\left.\frac{d^2I}{dE^2}\right|_{E_r} \tag{1}$$

Figure 1(c) displays this function for a fixed modulation potential. Near the crossover point (E_c), the second harmonic is proportional to the retarding potential (E_r),

$$i_2(E_r) = g(E_r + \phi - E_g) \tag{2}$$

where g is the proportionality constant, E_g is the gun potential, and ϕ is the work function of the surface. To reflect work function changes, either the gun potential or the retarding potential is modified so that the second harmonic remains constant.

Using these principles, Nathan and Hopkins[3] developed an ac method to monitor work function changes continuously. The retarding potential is varied to reflect the CPD ($\Delta\phi$), and, if the experimental conditions are chosen carefully, the change in the retarding potential is equal to the CPD. In the present work, the gun potential, rather than the retarding potential,

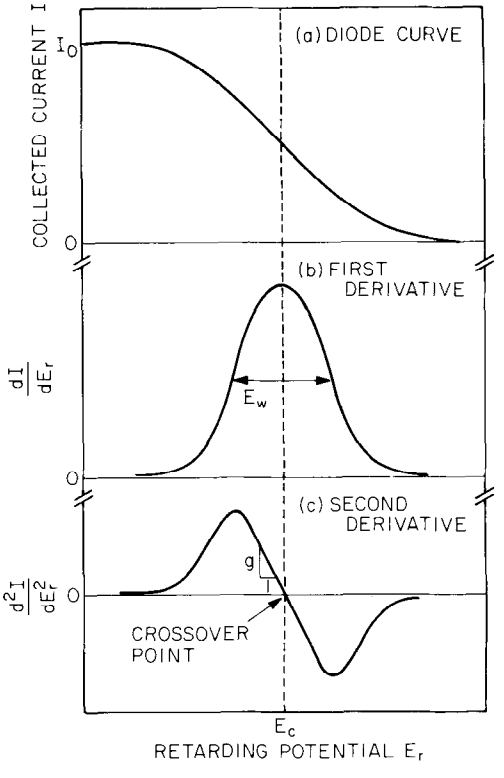

FIG. 1 The diode curve and its derivatives.

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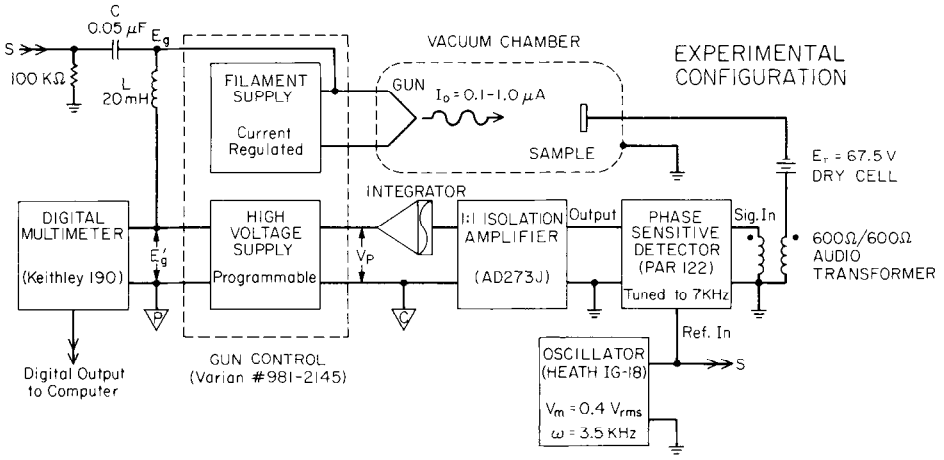

FIG. 2. Experimental configuration.

is varied to reflect the CPD, for this scheme could be implemented more easily with the existing experimental equipment. Moreover, the gun potential is varied so that the CPD is equal to the change in gun potential.

EXPERIMENTAL CONFIGURATION

Figure 2 diagrams this continuous diode method. Throughout an experiment, the change in gun potential is equal to the work function change. Several components in the diagram—an electron gun with a control unit, a phase sensitive detector, an audio oscillator, and a digital multimeter—are used routinely in commercial LEED/Auger systems with derivative detection. The filament and high-voltage power supplies are components of the gun control unit (Varian No. 981-2145), which has two noteworthy features. First, the gun current is regulated by maintaining a small constant potential (E_p) between point P and ground. Second, the high voltage supply is programmable. A 0–10 V programming signal (V_p) produces a proportional change in the potential E'_g. The gun potential is the sum of E_p and E'_g. Since this method measures differences in the potential, E_p may be ignored. The most severe requirement of this method is that the gun potential must be programmable.

The details of the measuring scheme are the following. A sinusoidal voltage is superimposed on the output of the high voltage supply through the network of L and C.[7] This modulates the gun potential as well as the potentials of the lens elements in the gun. In principle, this technique introduces less harmonic distortion to the gun current than that produced by modulating the gun potential only, although both techniques yield comparable experimental results. A fraction of the current is reflected to ground by the retarding potential, while the remainder arrives at the sample. Since the dc current would overload the phase sensitive detector, this unwanted signal is removed by the audio transformer. The second harmonic is amplified selectively by the detector. The detector output serves as an error signal to adjust the gun potential through the programming voltage (V_p). The CPD is equal to the change in gun potential compared to its initial value. A computer monitors this potential through a digital multimeter.[8]

Since the programming potential is referenced to a point C that is several volts above ground, an isolation amplifier tranduces the error signal between the reference points. This isolation amplifier is the only special component which has been added to the conventional LEED/Auger system. It is not used if the gun voltage is programmable from ground. The integrator, constructed from an FET operational amplifier, has two functions: filtering noise and providing high gain at low frequencies. This component is crucial in reducing tracking errors in the gun potential. Both the integrator and the isolation amplifier are powered by the gun control unit.

Various parameters affect the measured CPD through the open-loop gain (A). During closed loop operation, the gun potential tracks the sum of the retarding potential and the work function of the sample according to the relation

$$E_g = A(E_r + \phi)/(A + 1) \tag{3}$$

The open-loop gain is the product of the following factors: the slope of the second harmonic near the crossover point (g), the transimpedance of the audio transformer (Z), the gain of the phase sensitive detector at resonance (G_p), the pass function of the integrator ($1/\tau s$), and the gain for programming the high voltage supply (G_g)

$$A = gZ\,G_p\,G_g/\tau s \tag{4}$$

where s is the complex frequency in rad s^{-1}.

Two effects, not represented in Eq. (4), limit the practical values for the open-loop gain. The integrator has a finite gain at the low frequencies. To insure that the CPD is measured accurately, other gain parameters should be increased. However, these cannot be increased indefinitely without producing an instability, for poles and zeros associated with programming the high voltage supply introduce phase shifts. Open-loop gains (A) from $10/s$ to $1000/s$ were used in this work. The time constant of the integrator (τ) was fixed at one second and delimited the range of useful gains that could be selected on the phase sensitive detector. Since the response time of a digital multimeter is on the order of 0.1 s, the open-loop gain does not limit the rate of data acquisition.

In setting up this procedure, the retarding potential is fixed so that the diode curve does not change shape if the retarding potential is varied by several volts. The device which provides the retarding potential should be selected carefully. Instabilities in this potential appear directly in the measured CPD.

When a carbon or mercury cell battery supplies the retarding potential, measurements are reproducible within 10 meV, and noise margins are 5 meV. Noise is minimized best by maximizing the value of g in Eq. (2). Hence, the gun is sharply focused, and both the modulation voltage and the gun current are large. With the loop severed at the output of the integrator, the phase and frequency of the phase sensitive detector are tuned to the second harmonic. When the detector is truly aligned, its maximum output is proportional to the square of the modulation voltage (V_m) for small voltages. This voltage should be set so that the necessary proportionality is maintained. Otherwise, the second harmonic will not reflect the second derivative of the diode curve accurately. If the phase sensitive detector can filter the dc output, the filter is not used because it introduces phase shifts that induce instability. The integrator alone provides adequate filtering. The zero adjustment on the detector nulls dc offsets in the measuring loop. When the offsets are nulled, the loop is closed, and the gun is switched on; its potential rises rapidly to that of the crossover point. During a measurement, the sample can be heated if the double modulation technique of Tracy and Rowe[2] is implemented.

PERFORMANCE EVALUATION

Work function changes for saturation coverages of oxygen and CO on the (110) surface of Ir at 300 K were measured both with the continuous method and with a static dc diode technique. The results were identical. The CPD was 0.44 eV for oxygen and 0.23 eV for CO. Although CO has a large cross section for electron beam dissociation, no dissociation occurred since the beam potential is retarded to a small value before it strikes the surface. The measured CPD did not vary with either the modulation potential or the beam current since the open loop gain (A) was chosen to be suitably large. The CPD for a saturation coverage of oxygen on Ir(110) was measured for small deviations of the angle between the beam and the surface from normal incidence. When the angle changed by $\pm 5°$, the measured CPD varied by approximately 10 meV, which is within the experimental error of the technique. In order to evaluate the homogeneity of the surface, the electron beam was focused, perpendicular to the crystal but at various positions on it. So long as the beam area ($\sim$1 mm^2) does not overlap the edge of the sample, the same CPD is measured.

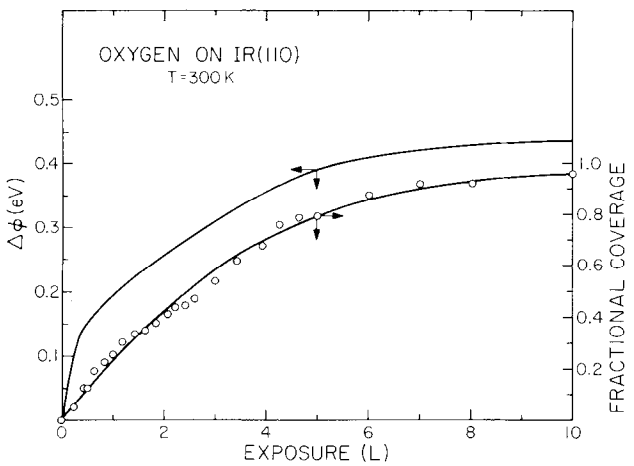

FIG. 3. Coverage and CPD as a function of oxygen exposure on Ir(110) at 300 K.

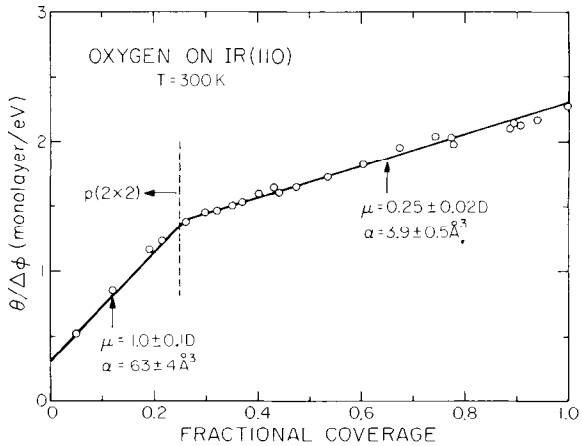

FIG. 4. Topping plot for oxygen adsorption on Ir(110) at 300 K.

This continuous diode technique was used to study the adsorption dynamics of oxygen on Ir(110) at 300 K. The CPD and fractional surface coverage are plotted as a function of oxygen exposure in Fig. 3. Coverages were measured by thermal desorption mass spectrometry. Surface coverage and CPD measurements are related through a Topping plot[9] in order to determine the normal components of both the dipole moment and the polarizability of the adsorbate for a fixed substrate temperature. In this Topping construction, the surface coverage is plotted as a function of the quotient of surface coverage and work function change. Results for oxygen adsorption at 300 K are shown in Fig. 4. For a surface coverage less than 0.25 ML, the dipole moment is 1.0 ± 0.1 D (1 D $\equiv 10^{-18}$ esu cm) and the polarizability is 63 ± 3 Å^3. For higher surface coverages, the dipole moment is 0.25 ± 0.02 D, and the polarizability is 3.7 ± 0.6 Å^3. The discontinuity in slope of the Topping plot at 0.25 ML is atttributed to an alteration of the overlayer structure. At that point, an oxygen $p(2 \times 2)$ LEED structure appears with maximum intensity, but vanishes at higher surface coverages. The details of the interaction of oxygen with Ir(110) are discussed elsewhere.[10]

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[5]A continuous dc method was implemented in this work. Although the method produced consistent and accurate CPD measurements, a thermocouple on the sample could not be read during an experiment since noise from the digital multimeter altered the reading.

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[7]A transformer with high voltage isolation can replace the LC network. The output impedance of the high voltage supply fixes the pass characteristic of this network. The signal at the output of the high voltage supply is equal to the reference signal up to 1 Hz. For higher frequencies, a single pole attenuates the output signal by 6 dB per octave.

[8]This computer, a PDP-11/10, performs several functions. The interfacing is detailed in: J. L. Taylor, Ph.D. Thesis (California Institute of Technology, 1978).

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